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(54) Title: ADHESIVE COMPOSITIONS AND THEIR PRECURSORS (57) Abstract An adhesive composition comprising a resin component containing a thermoplastic resin, an epoxy resin and a curing agent, characterized in that said thermoplastic resin contains a pressure sensitive adhesive polymer; and said resin component contains an inorganic colloid dispersed therein. A precursor for the adhesive composition is also disclosed.		

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ADHESIVE COMPOSITIONS AND THEIR PRECURSORSBACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to an adhesive composition comprising, as a base, a resin component containing a thermoplastic resin, an epoxy resin and a curing agent, and an adhesive composition precursor as a raw material of the adhesive composition.

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Description of the Related Art

As an adhesive film for FPC (flexible printed circuit board) protective film, an adhesive composition composed of a combination of various thermoplastic resins and a thermosetting epoxy resin has been known (see, for example, Japanese Unexamined Patent Publication (Kokai) Nos. 9-132710, 9-125037, 6-256746, 5-339556, 5-5085, 3-6280, 2-145676, 62-274690, 60-130666, 1-135844 and 61-43550).

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Among the adhesive films disclosed in the above publications, an adhesive film formed from a composition comprising a phenoxy resin and/or an acrylic adhesive polymer as the thermoplastic resin, an epoxy resin and a curing agent is comparatively superior in properties such as heat resistance, adhesion to metal and the like, and has hitherto been considered to be particularly useful. It is also disclosed in the above publications to employ a polyester polyol resin and various elastomers as the thermoplastic resin. As the curing agent, dicyandiamide is frequently used because of its excellent curing potential.

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It is preferred that the acrylic adhesive polymer include a carboxyl group, a hydroxyl group or an epoxy group in the molecule. For example, Japanese Unexamined Patent Publication (Kokai) Nos. 6-256746 and 5-339556 disclose compositions that reportedly have improved "repairing properties" due to a continuous epoxy resin phase and a dispersed phase of a phenoxy resin and a acrylic polymer. "Repairing properties" means that when circuit parts or circuits as

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the adherend are defective, the adhesive film can be easily removed from the adherend. After removing the adhesive film, non-defective circuit parts or circuits can be adhered to reconstruct the circuit. Accordingly, these publications do not disclose any means for effectively improving dimensional stability, impact resistance, flowability at the time of thermal bonding (preventing a flow large enough to cause squeeze-out), and adhesion.

It is known that the nonflammability of a resin composition can be improved by adding a combination of a brominated epoxy resin and antimony pentaoxide. See, for example, U.S. Patent Nos. 5,639,808; 4,105,622; 5,290,835; 5,221,704; 5,098,781; 5,681,879; 5,034,439; 5,180,767; 5,308,565; 5,719,225; and 5,536,970. According to the literature, a nonflammable composition is normally formed by mixing an antimony pentaoxide powder with the other resin component. The antimony pentaoxide powder is comparatively inexpensive, and its average particle diameter is normally not less than 0.5 μm .

Adhesive compositions comprising a thermoplastic resin, an epoxy resin and dicyandiamide have a drawback in that the stress produced during the heat curing process causes a large dimensional change. While reducing the dimensional change (i.e., improving the dimensional stability) is required for FPC protective film applications, it is very difficult to meet this requirement.

If the adhesive composition contains antimony pentaoxide powder, the antimony pentaoxide is liable to be sedimented, due to its specific gravity, in a liquid mixture of the antimony pentaoxide, other resin component and solvent. It is difficult to obtain a uniform mixture. A non-uniform mixture reduces dimensional stability and adhesion, resulting in a drastic deterioration in the composition's utility as the adhesive for FPC protective film.

Conventional adhesive films are not intended to:

- (i) reduce the flowability of the adhesive at the time of thermal bonding, so as to prevent squeeze-out of the adhesive after bonding (e.g. flow into the area to be soldered, thereby coating that area); and
- (ii) improve the impact resistance of the adhesive film (before curing is complete), thereby preventing breaking (e.g. cracking, etc.) when a film having a

predetermined shape and size is punched out in accordance with the part to be bonded. Conventional adhesive films do not disclose any means for solving these problems.

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SUMMARY OF THE INVENTION

The present invention provides an adhesive composition comprising a thermoplastic resin, an epoxy resin and a curing agent, and having improved utility as an adhesive for FPC protective film, particularly with respect to properties such as dimensional stability, impact resistance, flow resistance (resistance to flow) at
10 the time of thermal bonding, and adhesion.

The present invention also provides an adhesive composition precursor that can be advantageously used to provide such adhesive compositions.

In one aspect, the present invention provides an adhesive composition comprising a resin component containing a thermoplastic resin, an epoxy resin and
15 a curing agent, wherein:

said thermoplastic resin contains a pressure sensitive adhesive polymer; and
said resin component contains an inorganic colloid dispersed therein.

In the adhesive composition of the present invention, preferably, the epoxy resin contains a brominated epoxy resin;

20 said inorganic colloid is a colloid of antimony pentaoxide; and
the total amount of said brominated epoxy resin and said colloid of antimony pentaoxide is within the range from 13 to 60% by weight, based on the total amount of said adhesive composition.

In another aspect, the present invention provides an adhesive composition precursor which gives such an adhesive composition after drying. It comprises:
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- (i) the aforementioned resin component; and
- (ii) an inorganic particle sol containing a dispersion medium and aforementioned inorganic colloid dispersed in said dispersion medium.

A preferred method for producing the above adhesive comprises:

30 (a) mixing a first resin solution obtained by dissolving an epoxy resin, a curing agent, and an optionally added thermoplastic resin other than a pressure

sensitive adhesive polymer in a first solvent, with a second resin solution obtained by dissolving a pressure sensitive adhesive polymer in a second solvent to form a matrix resin solution; and

- (b) adding an inorganic colloid sol to the matrix resin solution, followed by mixing to obtain an adhesive composition precursor of the formed uniform dispersion. The first and second solvents will be described in detail hereinafter.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The adhesive composition of the present invention is a composition comprising, as a base, a resin component containing a thermoplastic resin, an epoxy resin and a curing agent, containing a pressure sensitive adhesive polymer as the thermoplastic resin and an inorganic colloid dispersed in the resin component. The adhesive compositions of the present invention can effectively improve the following properties:

- (a) dimensional stability, particularly dimensional stability after a heat treatment (for the purpose of completing the cure) which is carried out after thermal bonding;
- (b) impact resistance (particularly before the completion of cure);
- (c) flow resistance at the time of thermal bonding (e.g. prevention of adhesive squeeze-out into the area to be soldered); and
- (d) adhesion.

Dimensional stability can be improved to such a degree that the dimensional change is not more than 0.1%. The impact resistance can be improved to such a degree that when a hole having a diameter of 10 mm is punched in a polymer film-adhesive film laminate (formed by applying an adhesive composition to a polymer film), no crack occurs at the periphery of the hole. The flow resistance at the time of thermal bonding can be improved to such a degree that when a hole (1 mm² X 1 mm²) is bored in an adhesive film, and a rolled copper foil having a thickness of 30 μm is placed on the adhesive film to cover the hole and then thermally bonded at 120°C under a pressure of 38 kg/cm² for 1 minute,

the squeeze-out of the adhesive composition at the periphery of the hole is not more than 0.6 mm in length. The adhesion can be improved to such a degree that when an adhesive composition is used for bonding between a metallic foil such as copper foil and a film of a polymer such as polyimide, the adhesion strength can be effectively enhanced (e.g. peel strength can be increased to 500 kg/cm or more).

One preferred aspect of the present invention provides an adhesive composition wherein: the epoxy resin contains a brominated epoxy resin; the inorganic colloid is a colloid of antimony pentaoxide; and the total amount of the brominated epoxy resin and the colloid of antimony pentaoxide is within the range from 13 to 60% by weight based on the total amount of all of the resin ingredients.

The term "brominated epoxy resin," as used herein, refers to an epoxy resin wherein a bromine atom is introduced into the molecule. For example, the brominated epoxy resin has a structure in which one or more hydrogen atoms of the phenyl ring in a molecule of a bisphenol type epoxy resin is substituted with a bromine atom. The epoxy resin other than the "brominated epoxy resin" is particularly referred to as a "non-brominated epoxy resin" in the specification of the present application, and is distinguished from the brominated epoxy resin.

In another aspect, the present invention resides in the combined use of an inorganic colloid and a pressure sensitive adhesive polymer in an adhesive composition that is based on an epoxy resin and a curing agent. Particularly, the inorganic colloid can improve the dimensional stability and flow resistance during thermal bonding. Preferably, the inorganic particles are in the form of a colloid, which will be defined hereinafter. The pressure sensitive adhesive polymer can cooperate with the inorganic colloid to improve dimensional stability and flow resistance, and synergistically combines with the inorganic colloid to improve impact resistance. Further, the inorganic colloid and the pressure sensitive adhesive polymer can improve the excellent adhesion of the adhesive composition based on the epoxy resin and the curing agent.

The adhesive composition in accordance with this preferred aspect of the present invention is sufficiently nonflammable to pass level V0 of Underwriter's Laboratories, Inc. specification UL-94. In such an adhesive composition, when the

total amount of the brominated epoxy resin and the colloid of antimony pentaoxide is less than 13% by weight, based on the total amount of the adhesive composition, level V0 is not passed. On the other hand, when it exceeds 60% by weight, the peel strength is lowered.

5 The term "resin component" refers to a mixture of an epoxy resin, a curing agent, a pressure sensitive adhesive polymer, and an optional additional component. The additional, optional component includes (i) thermoplastic resins such as phenoxy resin, polyester polyol, etc., (ii) curing accelerators, and (iii) additives such as tackifier, plasticizer, etc., but is not limited thereto.

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Pressure Sensitive Adhesive Polymer

 The pressure sensitive adhesive polymer forms a fine phase separation structure having a size (e.g. diameter in the case of a spherical form) of about 1 nm to 1 μ m in the adhesive composition. This fine structure and molecules of the
15 other polymers (e.g. epoxy resin, phenoxy resin, etc.) in the adhesive composition are entangled in each other, thereby making it possible to improve the flow resistance at the time of thermal bonding and impact resistance at the same time. If the fine structure has configurations other than a spherical form, such as an elliptical form or an indefinite form, the size of such fine structures should be
20 measured as the longest dimension thereof, for example, the longitudinal axis in elliptical particles.

 The content of the pressure sensitive adhesive polymer is not limited so long as the effect on the present invention is not adversely affected, but is normally from 0.1 to 25% by weight, based on the total amount of the adhesive composition.

25 When the content is too small, the dimensional stability, impact resistance, flow resistance, and adhesion may not be improved. On the other hand, when the content is too large, other features of the adhesive composition (e.g. nonflammability) are likely to be reduced. From this point of view, the preferred content of the pressure sensitive adhesive polymer is within the range of 1 to 10%
30 by weight, based on the total amount of the adhesive composition.

The term "pressure sensitive adhesive polymer" refers to a polymer showing pressure sensitive adhesion at a normal temperature (about 25°C). An acrylic polymer is preferred because it can effectively enhance adhesion. As the acrylic polymer, an alkyl acrylate-aromatic acrylate copolymer is preferred because the aromatic acrylate in the polymer molecule has good compatibility with the epoxy resin and can easily exert an interaction of entanglement. When the adhesive composition contains a phenoxy resin, the alkyl acrylate-aromatic acrylate copolymer has a good interaction with the phenoxy resin, thereby making it possible to improve the flow resistance at the time of thermal bonding as well as impact resistance.

When using the alkyl acrylate-aromatic acrylate copolymer as the acrylic polymer, the weight ratio of the alkyl acrylate (A) to the aromatic acrylate (P) in the copolymer, i.e. (A:P), is not specifically limited so long as the copolymer shows pressure sensitive adhesion, but is preferably from 30:70 to 99:1, and particularly preferably from 40:50 to 90:10. When the amount of the aromatic acrylate in the copolymer is too small, the flow resistance at the time of thermal bonding and impact resistance are likely to be reduced. On the other hand, when the amount of the aromatic acrylate is too large, the dimensional stability is likely to be reduced. Specific examples of the alkyl acrylate include butyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, and the like. Specific examples of the aromatic acrylate include phenoxyalkyl acrylate and the like.

The acrylic polymer can also contain other monomer units in place of or together with the alkyl acrylate or aromatic acrylate. These monomer units are, for example, alkyl methacrylate, (meth)acrylic carboxylic acid (e.g. acrylic acid, etc.), (meth)acrylic polycarboxylic anhydride, and alkoxy (meth)acrylate (e.g. acetoacetoxy acrylate, etc.). However, when the adherend to which the adhesive composition is applied is metal, it is preferred that the acrylic polymer not contain substantial amounts of a carboxylic acid so as to prevent corrosion of the adherend.

Inorganic Colloid

Since the inorganic colloid is normally contained in the dispersion in the form of colloidal particles, the colloidal particles are not sedimented by specific gravity and can be stably dispersed. Accordingly, the adhesive composition of the present invention formed by drying such a dispersion can achieve a state where the different components are uniformly mixed, thereby making it possible to improve peel strength and dimensional stability.

Also, the content of the inorganic colloid in the adhesive composition is not specifically limited so long as the effect of the present invention is not adversely affected, but is normally within the range of from 1 to 50% by weight. When the content is less than 1% by weight, the dimensional stability is likely to be reduced. On the other hand, when the content exceeds 50% by weight, the peel strength is likely to be reduced. The preferred content of the inorganic colloid is within the range of 2 to 45% by weight, based on the total weight of the adhesive composition.

The term "inorganic colloid" normally refers to fine particles having an average particle diameter within the range of 1 to 100 nm. For example, preferred are those obtained by mixing an inorganic particle sol with a resin component and dispersing the sol in the resin component. The inorganic particle sol is normally a mixture of (i) a dispersion medium and (ii) the inorganic colloid dispersed in the dispersion medium. As the inorganic particle sol, there can be used antimony pentaoxide sol, silica sol or the like.

Resin Component

The resin component normally comprises the following three components:

- 1) a thermoplastic resin containing a pressure sensitive adhesive polymer;
- 2) an epoxy resin; and
- 3) a curing agent.

In one preferred aspect of the present invention, the resin component comprises:

- (a) a phenoxy resin;
- (b) a non-brominated epoxy resin;
- (c) a brominated epoxy resin;
- (d) a pressure sensitive adhesive polymer; and
- (e) a curing agent.

The components other than the pressure sensitive adhesive polymer (d), which has already been explained, will be described in detail below.

The phenoxy resin (a) is one of the components of the thermoplastic resin that contributes to improved adhesive strength. Regarding the phenoxy resin, the intermolecular attraction between a hydroxyl group of a polymer molecule constituting the phenoxy resin and the flexibility of the resin itself contributes to an improved peel strength. The kind and amount of the phenoxy resin are preferably selected so that the glass transition temperature of the cured composition is at least 70°C. Consequently, the dynamic folding resistance of the cured composition is enhanced, thereby making it possible to effectively prevent breakage and peel-off of the adhesive layer in use.

The non-brominated epoxy resin (b) increases the glass transition temperature of the cured composition by reacting with a curing agent such as dicyandiamide. A high glass transition temperature is advantageous for enhancing the heat resistance. The kind and amount of the non-brominated epoxy resin are also preferably selected so that so that the glass transition temperature of the cured composition does not reach 70°C or less. As the non-brominated epoxy resin, for example, there can be used epoxy resins such as bisphenol A epoxy resin, bisphenol F epoxy resin, cresylic novolak epoxy resin, phenolic novolak epoxy resin and the like. When using the brominated epoxy resin, the non-brominated epoxy resin is not an essential component. However, both types of epoxy resins are preferably included to enhance both adhesive strength and nonflammability.

The brominated epoxy resin (c) enhances the nonflammability of the composition. The brominated epoxy resin also enhances the solubility of the phenoxy resin in a specific solvent (e.g. a mixed solvent containing methyl ethyl ketone and methanol). The mixed solvent containing methyl ethyl ketone and

methanol has a comparatively large evaporation rate. Accordingly, a combination of the brominated epoxy resin and phenoxy resin is preferred for reducing the amount of the residual solvent in the adhesive composition (e.g. adhesive film, etc.) after drying and for providing a uniform mixture of the respective components. The brominated epoxy resin (like the non-brominated epoxy resin) reacts with the curing agent. The kind and amount of the brominated epoxy resin are preferably selected so that a good balance between the nonflammability of the composition, the solubility of the phenoxy resin, and the glass transition temperature (exceeding 70°C) of the composition after curing can be obtained.

The curing agent (e) is a compound that can react with at least an epoxy resin to cure or crosslink the same. Preferably the curing agent is dicyandiamide or its derivatives. Dicyandiamide and its derivatives are superior in curing potential, and effectively enhance the storage stability of the adhesive composition and its precursor. The kind and amount of the curing agent are also preferably selected similar to the other resin components.

In addition to components (a) to (e), the resin component can contain various optional components. The amount of these optional components is also preferably selected similar to the above other resin components.

The content of the resin component other than the pressure sensitive adhesive polymer contained in the adhesive composition is not specifically limited so long as the effect of the present invention is not adversely affected. For example, explaining the case where the phenoxy resin is the thermoplastic resin, the content of (a) the phenoxy resin, (b) the non-brominated epoxy resin, (c) the brominated epoxy resin, and (d) the curing agent, each based on the total amount of all the resin ingredients, are respectively from 40 to 91.5% by weight (a), from 4 to 40% by weight (b), from 4 to 50% by weight (c) and from 0.1 to 7% by weight (d). More preferably the composition includes from 50 to 90% by weight (a), from 5 to 35% by weight (b), from 5 to 40% by weight (c), and from 0.5 to 5% by weight (d). With such a constitution the components are uniformly mixed in the adhesive composition (after drying) that is formed by using these resin components and a solvent (e.g. methyl ethyl ketone, methanol, ethyl alcohol, etc.).

Adhesive Composition Precursor

The adhesive composition precursor is a raw material of the adhesive composition that provides the adhesive composition of the present invention. This precursor is normally composed of the resin component, particles of an inorganic colloid such as a colloid of antimony pentaoxide, and a solvent.

The inorganic colloid is normally mixed with the other components in the form of a sol, and is uniformly dispersed in a vehicle of the resin components and solvent. As the sol, those prepared by dispersing colloidal particles in a dispersion medium containing an organic solvent are normally used. The solvent of the sol is preferably selected considering the solubility to the resin components. Among them, methyl ethyl ketone is particularly preferred because the dispersion stability of the sol (particles) in the precursor is not likely to be deteriorated. The concentration of the inorganic colloid in the adhesive composition precursor is normally within the range of 1 to 50% by weight.

The adhesive composition precursor can be produced by various methods, and the method of producing the same will be described in detail below with reference to a case using a colloid of antimony pentaoxide as the inorganic colloid.

Among the resin components, an epoxy resin, a curing agent and a thermoplastic resin other than "a pressure sensitive adhesive polymer", such as phenoxy resin, which is optionally added, are dissolved in a first solvent to prepare a first resin solution. The pressure sensitive adhesive polymer is dissolved in a second solvent to prepare a second resin solution. The first and second resin solutions are mixed to prepare a matrix resin solution. Mixing can be carried out using, for example, a high-speed mixer, a planetary mixer, a homomixer, sand mill or the like. The solid content of the matrix resin solution is normally within the range of 5 to 70% by weight.

Furthermore, an antimony pentaoxide sol is added to the matrix resin solution to prepare a uniform dispersion, using a suitable mixing means such as those described for preparing the matrix resin solution. The uniform dispersion thus obtained is the adhesive composition precursor. According to such a

production method, there can be easily prepared a precursor containing antimony pentaoxide particles that are uniformly and stably dispersed in the resin components.

The matrix resin solution preferably exhibits microphase separation.

5 Depending on the kind and amount of the components contained in the first and second resin solutions, the first and second solvents are preferably different. Microphase separation in the adhesive composition formed by drying the precursor makes it possible to further enhance the dimensional stability, impact resistance, flow resistance at the time of thermal bonding, etc. of the adhesive composition.

10 The microphase separated structure in the adhesive composition is a structure wherein one phase (the dispersed phase) forms islands having a size (diameter) of not more than 1 μm that are uniformly dispersed in a continuous sea (the continuous phase). The dispersed phase preferably contains the pressure sensitive adhesive polymer. In this case, the epoxy resin and curing agent are normally present in the continuous phase. When using a thermoplastic resin other than the pressure sensitive adhesive polymer (e.g., the phenoxy resin) the thermoplastic resin is preferably present in the continuous phase. In this case, the epoxy resin and curing agent may be present in the continuous phase or dispersed phase.

20 The solvent for the first resin solution should be a good solvent for the curing agent and the thermoplastic resin other than the pressure sensitive adhesive polymer (e.g., phenoxy resin). The solvent for the second resin solution should be a good solvent for the pressure sensitive adhesive polymer, but a poor solvent for the epoxy resin, curing agent and phenoxy resin. For example, when the pressure sensitive adhesive polymer is an acrylic polymer, the first solvent is a mixture of methyl ethyl ketone (MEK) and methanol, and the second solvent is (i) an ester solvent alone, such as ethyl acetate, butyl acetate or the like, or (ii) a mixture of an ester solvent and a sub-solvent of the first solvent (e.g., toluene, isopropanol, acetone, MEK or blends thereof). When the second solvent is a mixture of an ester solvent and a sub-solvent, the weight ratio of the ester solvent (E) to the sub-solvent (S), i.e. (E:S), is within the range from 100:0 to 55:45.

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The weight ratio of methanol to MEK in the first solvent is normally from 0.005 to 0.4. When the ratio is less than 0.005:1, the solubility of dicyandiamide is lowered. On the other hand, when the ratio exceeds 0.4:1, the solubility of the thermoplastic resin is lowered. In both cases, it becomes more difficult to
5 uniformly mix the components.

The first solvent may contain solvents other than methyl ethyl ketone and methanol. For example, it may contain alcohols such as ethanol, isopropyl alcohol, n-propyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, etc., or nitrogen-containing solvents such as acetonitrile, etc. Among these, ethanol has
10 good solubility to dicyandiamide, an evaporation rate lower than that of methyl ethyl ketone, and does not drastically reduce the evaporation rate of the mixed solvent. Accordingly, a uniform coating can be obtained without lowering the drying rate of the coating.

The adhesive composition precursor of the present invention is a dispersion
15 having excellent storage stability because the inorganic colloid is stably dispersed in the matrix resin solution. The precursor composition is a dispersion wherein the two resin solutions cause stable microphase separation. Accordingly, the adhesive film of the adhesive composition of the present invention can be easily formed by purchasing such a stable dispersion, storing the dispersion, and then applying and
20 drying it at the desired time.

The adhesive composition precursor can contain various additives as far as the effect of the present invention is not adversely affected. Suitable additives are, for example, surfactants, viscosity adjustors and the like.

25 Adhesive Film

The adhesive composition of the present invention can be used, for example, in the form of an adhesive film. The thickness of the film is normally within the range from 5 to 1,000 μm .

The adhesive film can be produced by various methods that involve
30 applying the adhesive composition precursor on a substrate and drying the precursor. As the applying means, there can be used the same means as in case of

producing a normal adhesive film. Examples of suitable applying means include a knife coater, a bar coater, a die coater, an extruder and the like. The drying condition is not specifically limited. However, drying is normally performed at a temperature of 60 to 100°C for several seconds to 1 hour so that the residual solvent does not remain and the curing reaction of the composition does not proceed excessively at the time of drying.

As the above substrate, there can be used plastic films such as polyimide film, polyester film, etc. and metal foils such as copper foil, aluminum foil, etc., but the invention is not limited to these. In this case, it is normally employed as an adhesive sheet or adhesive film comprising a layer of an adhesive film and a substrate. Using a release film as the substrate, the release film may be removed before use and an adhesive film alone can also be used.

The adhesive film is laminated on the adherend and bonding between them is completed by a thermal bonding operation including heating at 100 to 180°C for 0.1 to 2 minutes under a pressure of from 2 to 50 kg/cm². After the completion of the thermal bonding operation, the following heating operation at 150 to 180°C for 1 to 5 hours can also be performed. At the time of the thermal bonding operation, the thickness of the adhesive film is preferably adjusted so that squeeze-out of the composition component from the film end hardly arises. The thickness of the adhesive film is normally from 10 to 2,000 μm.

The formulation of the adhesive composition is preferably selected so that the tensile storage modulus at 60°C of the cured adhesive film is not less than 1010 dyn/cm². Consequently, it is possible to obtain an adhesive film having high dynamic folding resistance at 60°C, which is suitable as an adhesive for FPC protective film.

The adhesive for FPC protective film is preferably selected so that the shrinkage rate of the adhesive film after the completion of curing is not more than 0.1%. This shrinkage rate is a percentage of a reduction in size after curing to the size before curing.

EXAMPLES

The present invention will be described in more detail with reference to the following examples. It will be appreciated that the present invention is not limited to the following examples. In the following examples, "parts" are by weight unless
5 otherwise stated.

Example 1

(1) Preparation of adhesive composition precursor (dispersion) and formation of adhesive film.

10 First, 60 parts of a phenoxy resin (trade name: YP50S, number-average molecular weight: 1,180, weight average molecular weight: 58,600, manufactured by Tohto Kasei Co., Ltd.), 15 parts of a bisphenol A epoxy resin (trade name: YD128, epoxy equivalent = 370, manufactured by Tohto Kasei Co., Ltd.), 15 parts of a brominated epoxy resin (trade name YDB400, epoxy equivalent of about 400,
15 manufactured by Tohto Kasei Co., Ltd.), and 1.5 parts of dicyandiamide (Dicy) (trade name: Amicure GG1200, amine equivalent of 21, manufactured by Tohto Kasei Co., Ltd.) were dissolved in a mixed solvent containing 80 parts of methyl ethyl ketone and 35 parts of methanol. A uniform first resin solution was obtained.

Then, an acrylic pressure sensitive adhesive polymer solution, SKDyne™
20 (Model No. SK1309, manufactured by Sohken Kagaku Co., Ltd.) was prepared as a second resin solution. It was added to the whole first resin solution prepared as described above so that the solid content of the pressure sensitive adhesive polymer was 9.6 parts based on the total first resin solution, thereby obtaining a matrix resin solution wherein the components of the second resin solution caused microphase
25 separation and was stably dispersed in the first resin solution. The acrylic pressure sensitive adhesive polymer as the second resin solution is an acrylic acid unit-containing copolymer and can be available as a solution dissolved in a mixed solvent of ethyl acetate and toluene (65:35).

To the matrix resin solution prepared as described above, 20 parts of an
30 antimony pentaoxide sol (trade name: Sun Colloid AME-130, particle diameter: 5 to 50 nm, solid content: 30% by weight, dispersion medium: methyl ethyl ketone,

manufactured by Nissan Chemical Co., Ltd.) was added. An adhesive composition precursor of this example was obtained as a uniform dispersion. The composition of the resulting adhesive composition precursor is as described in Table 1 below for reference. The ratio of methanol (MeOH) to methyl ethyl ketone (MEK) in a solvent included in this adhesive composition precursor, i.e. MeOH/MEK was 0.37.

The adhesive composition precursor of this example was evaluated with respect to the dispersion stability. The results show that the formed microphase separation is stably maintained and the dispersion stability is good. The dispersion state was satisfactory enough to recover the original state by shaking several times by hand, even after 30 days.

Subsequently, the resulting dispersion was uniformly applied on a substrate film of any one of the following plastic films:

a PET film subjected to a releasing treatment or
a polyimide film (trade name: Kapton V, thickness: 25 μ m),
and then dried at 90°C for 30 minutes. An adhesive film with a substrate comprising a substrate film and, having applied thereon, an adhesive film comprising the adhesive composition of the present invention and having a thickness of 30 μ m, was thus obtained.

(2) Evaluation of characteristics of adhesive film

The characteristics of the resulting adhesive film were evaluated with respect to the following items (A) to (G) according to the procedures described below.

A. Dynamic viscoelasticity

After an adhesive film with a PET film was prepared as described above, the PET film was peeled off to obtain an adhesive composition (adhesive film alone). The adhesive film was sandwiched between two release papers and the resulting laminate was thermally bonded at 120°C under a pressure of 20 kg/cm² for 1 minute. Subsequently, the laminate was heat-treated at 170°C for 2 hours, thereby curing the adhesive film. The cured adhesive film was removed from the two release papers and was taken as a test piece. The minimum shear modulus

Gmin x 10⁻⁴ (dyn/cm²) of this test specimen was measured when the temperature was raised from 100 to 170°C at a rate of 40°C per minute. The device used for measuring the minimum shear modulus was a dynamic viscoelasticity measuring device, Model No.: RSAII, manufactured by Rheometric Co., and the measuring frequency was 6.28 rad/second.

B. Flow resistance of adhesive at the time of thermal bonding

After a generally circular through hole (1 mm² x 1 mm²) was bored in an adhesive film alone prepared in the same manner as that described in the above item (A), a rolled copper foil having a thickness of 30 μm was placed on the adhesive film so as to cover the hole and they were thermally bonded at 120°C under a pressure of 38 kg/cm² for 1 minute. At this time, the amount (length) of squeeze-out of the adhesive composition into the hole from the periphery of the hole was measured by using an optical microscope. It was taken as the flow resistance (unit:mm) at the time of thermal bonding. The smaller this value, the lesser the amount of squeeze-out and the better the flow resistance.

C. Dimensional stability

After an adhesive film with a polyimide film was prepared as described above, a rectangular scratch mark (about 70 mm x about 35 mm) was formed on the polyimide surface of the adhesive film and the length of the long side was measured. Then, the same film, Kapton V (trade name, aforecited), as that described above was laminated on the adhesive surface of the adhesive film. The resulting laminate was thermally bonded at 120°C under a pressure of 10 kg/cm² for 1 minute. Subsequently, the laminate was heat-treated at 170°C for 2 hours to obtain a test piece. After the test piece was allowed to stand at room temperature for one additional hour, the length of the long side of the scratch mark on the test piece was measured again and a ratio (%) of the changed length to the length before thermal bonding was taken as a dimensional change (%). When the dimensional change shows a negative value, it means that the test piece shrank.

D. Glass transition temperature (Tg)

An adhesive film alone was post-cured at 150°C for 3 hours and was taken as a test piece. In the same manner as that described in the above item (A), the

tensile modulus ($E' + E''$) was measured and the temperature at which $\tan \delta$ (E' / E'') becomes maximum was taken as the glass transition temperature T_g ($^{\circ}\text{C}$). The measuring frequency was 6.28 rad/second.

E. Solder heat resistance

5 An adhesive film alone was placed on a rolled copper foil having a thickness of 30 μm , and they were thermally bonded at 120 $^{\circ}\text{C}$ under a pressure of 20 kg/cm^2 for 1 minute and then post-cured at 150 $^{\circ}\text{C}$ for 3 hours to obtain a test piece. This test piece was allowed to stand on molten solder at 260 $^{\circ}\text{C}$. The case where foaming did not occur was judged as "Pass" (i.e., passed the solder heat resistance test), whereas, the case where foaming occurred was judged as a
10 "Failure" (i.e., failed the solder heat resistance test).

F. Adhesive strength

A rolled copper foil having a thickness of 30 μm was laminated on the adhesive surface of an adhesive film with a polyimide film prepared in the same
15 manner as described above, and they were thermally bonded at 120 $^{\circ}\text{C}$ under a pressure of 20 kg/cm^2 for 1 minute. Subsequently, the resulting laminate was heat-treated at 170 $^{\circ}\text{C}$ for 2 hours to obtain a test piece. The copper foil of this test piece was peeled off at a peel angle of 180 $^{\circ}$ and a peel rate of 50 mm/min and the integrated average value of the resulting value was taken as an adhesive strength
20 (peel adhesive strength, g/cm).

G. Die punching properties

After a through hole having a diameter of 10 mm was formed in an adhesive film with a polyimide film prepared in the same manner as described above by punching out using a punch cutter, the periphery of the through hole was
25 observed by an optical microscope (magnification: x 50). The case where a crack was observed was judged "NG" (i.e., it failed), whereas, the case where crack was not observed was judged "OK" (i.e., it passed).

The evaluation results of the characteristics described in the above items (A) to (G) are summarized in Table 1 below.

30 Furthermore, the characteristics of the resulting adhesive film were also evaluated with respect to the following items.

H. Nonflammability

An adhesive film alone was evaluated with the respect to the nonflammability by the method in accordance with the specification UL94. As a result, the adhesive film of this example satisfied the level V0 and showed that the nonflammability is good.

I. Microphase separated structure

The adhesive composition precursor and adhesive film of this example were respectively observed by an optical microscope (magnification: x 500). As a result, it has been found that both of them have a microphase separated structure, wherein a fine "separated phase" having a size of submicron order or less is uniformly dispersed in a "continuous phase". It is considered that such a microphase separated structure effectively contribute to an improvement in dimensional stability, impact resistance (die punching properties) and flowability at the time of thermal bonding.

Reference Example 1 and Reference Example 2

These examples are reference examples carried out for comparison with Example 1.

In the same manner as that described in Example 1, except for replacing the ethyl acetate/toluene mixed solvent of the second resin solution by methyl ethyl ketone alone (Reference Example 1) and toluene alone (Reference Example 2), an adhesive composition precursor of this example was prepared. The adhesive composition precursor of this example gave an adhesive film having the same performances as those of Example 1 when using it immediately after preparation. However, the storage stability was not good and the same microphase separated structure as that of Example 1 could be maintained only for several hours.

Example 2

In the same manner as that described in Example 1, except for replacing the kind and content of the pressure sensitive adhesive polymer as shown in Table 1 below, an adhesive composition precursor and adhesive film of this example were

prepared. The pressure sensitive adhesive polymer used in this example is that (trial preparation No. EX01) obtained by reacting in an ethyl acetate solution according to a solution polymerization method, and was a copolymer of 2-methylbutyl acrylate and an acrylic acid (weight ratio: 90:10). In this example, an ethyl acetate solution having a concentration of 30% by weight was used as a second resin solution.

The adhesive composition precursor of this example had good dispersion stability, similar to Example 1. The adhesive composition precursor and adhesive film of this example had the same microphase separated structure as that of Example 1. Furthermore, the adhesive film of this case was evaluated in the same manner as that described in Example 1. The results are shown in Table 1 below.

Examples 3 to 14

In the same manner as that described in Example 1, except for replacing the kind and content of the respective resin components as shown in Table 1 below, an adhesive composition precursor and adhesive film (adhesive composition) of each example were prepared.

The adhesive composition precursor of each example had good dispersion stability, similar to Example 1. The adhesive composition precursor and adhesive film of each example had the same microphase separated structure as that of Example 1. Furthermore, the adhesive film of each example was evaluated in the same manner as that described in Example 1. The results are shown in Table 1 below. The details of the resin components used newly in each example are as listed below.

Polyester polyol containing phenoxy resin

PKHM30: polyester polyol-containing phenoxy resin, (trade name: PKHM-30, containing about 30% by weight of polyester polyol, manufactured by Union Carbide Co.).

Pressure sensitive adhesive polymer (second resin solution)

Examples 3 and 4: product obtained by solution polymerization (trial preparation No. EX02), copolymer of phenoxyethyl acrylate and acrylic acid (weight ratio 9:1).

5 Examples 5 and 6: the same one as that of Example 1 is used.

Example 7: product obtained by solution polymerization (trial preparation No. EX03), copolymer of ethyl acrylate and acrylic acid (weight ratio = 9:1).

10 Example 8: copolymer having a hydroxyl group in the molecule, SK1435 manufactured by Sohkent Kagaku Co., Ltd., available as a solution containing a mixed solvent of ethyl acetate and toluene (59:41).

Example 9: the same one as that of Example 1 is used.

Example 10: product obtained by solution polymerization (trial preparation No. EX04), copolymer of butyl acrylate and 4-methacryloyloxyethyltrimellitic anhydride (weight ratio = 90:10).

15 Example 11: product obtained by solution polymerization (trial preparation No. EX05), copolymer of butyl acrylate and acetoacetoxyethyl methacrylate (weight ratio = 80:20).

20 Exmple 12: product obtained by solution polymerization (trial preparation No. EX06), copolymer of 2-ethylhexyl acrylate and phenoxyethyl acrylate (weight ratio = 80:20).

Example 13: product obtained by solution polymerization (trial preparation No. EX07), copolymer of butyl acrylate and phenoxyethyl acrylate (weight ratio 50:50).

25 Example 14: product obtained by solution polymerization (trial preparation No. EX08), copolymer of acrylate macromer and phenoxyethyl acrylate (weight ratio = 50:50).

Comparative Examples 1 and 2

30 In the same manner as that described in Example 1, except for replacing the kind and content of the respective resin components as shown in Table 1 below, an

adhesive composition precursor and adhesive film (adhesive composition) of each example was prepared.

5 The adhesive film of each example was evaluated in the same manner as that described in Example 1. The results are shown in Table 1 below. Since the pressure sensitive adhesive polymer is not used in these comparative examples, the die punching properties are particularly inferior to Examples 1 to 14.

Table 1

	YP50S (Parts)	PKHM3 0 (Parts)	YD128 (Parts)	YDB400 (Parts)	Dicy (Parts)	PSA polymer (Parts)	Gmin x 10 ⁻⁴ [dyn/cm ²]	Flow resistance of adhesive [mm]	Dimensional change [%]	Tg [°C]	Solder heat resistance [g/cm]	Adhesive strength [g/cm]	Die punching properties
Ex. 1	60	-	15	15	1.5	9.6	3.1	0.1	-0.04	89	Pass	650	OK
Ex. 2	60	-	15	15	1.5	10	2.9	0.1	-0.06	89	Pass	750	OK
Ex. 3	60	-	15	15	1.5	10.5	2.2	0.1	-0.07	89	Pass	1230	OK
Ex. 4	60	-	15	15	1.5	15	2.7	0.1	-0.08	89	Pass	520	OK
Ex. 5	60	-	15	15	1.5	6.4	3.0	0.1	-0.1	89	Pass	670	OK
Ex. 6	60	-	15	15	1.5	12.8	5.1	0.1	-0.1	89	Pass	500	OK
Ex. 7	60	-	15	15	1.5	9	3.0	0.1	-0.02	89	Pass	500	OK
Ex. 8	60	-	15	15	1.5	9	3.5	0.6	-0.05	89	Pass	1150	OK
Ex. 9	55	15	15	15	1.5	3	3.6	0.1	-0.04	89	Pass	500	OK
Ex. 10	55	15	15	15	1.5	3	4.6	0.3	-0.04	89	Pass	600	OK
Ex. 11	55	15	15	15	1.5	3	3.2	0.4	-0.04	89	Pass	780	OK
Ex. 12	55	15	15	15	1.5	3	2.9	0.1	-0.04	89	Pass	1030	OK
Ex. 13	55	15	15	15	1.5	3	3.0	0.2	-0.04	89	Pass	980	OK
Ex. 14	55	15	15	15	1.5	3	3.0	0.1	-0.04	89	Pass	930	OK
Comp. Ex. 1	70	-	20	10	3	-	1.1	0.1	-0.15	105	Pass	570	NG
Comp. Ex. 2	55	15	15	15	1.5	-	1.4	0.3	-0.05	74	Pass	1000	NG

As described above, according to the present invention, the dimensional stability after a heat treatment performed after thermal bonding, impact resistance before the completion of curing, flow resistance at the time of thermal bonding (e.g. prevention of cause squeeze-out onto the portion to be soldered), adhesion and nonflammability can be effectively enhanced in the adhesive composition. Accordingly, this adhesive composition can be advantageously used as an adhesive for FPC protective film.

CLAIMS

We claim:

1. An adhesive composition comprising a resin component containing
5 a thermoplastic resin, an epoxy resin and a curing agent, characterized in that:
said thermoplastic resin contains a pressure sensitive adhesive polymer; and
said resin component contains an inorganic colloid dispersed therein.

2. The adhesive composition according to claim 1, wherein said epoxy
10 resin contains a brominated epoxy resin;
said inorganic colloid is a colloid of antimony pentaoxide; and the total
amount of said brominated epoxy resin and said colloid of antimony pentaoxide is
within the range from 13 to 60% by weight based on the total amount of said
adhesive composition.

15

3. An adhesive composition precursor which gives the adhesive
composition of claim 1 after drying, comprising:

(i) an aforementioned resin component; and
(ii) an inorganic particle sol containing a dispersion medium and
20 aforementioned inorganic colloid dispersed in said dispersion medium.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/13486

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09J163/00 C09J133/00 C08K3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09J C08K C08L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 04, 31 March 1998 (1998-03-31) & JP 09 316365 A (PENTEL KK), 9 December 1997 (1997-12-09) abstract ---	1
X	EP 0 819 746 A (SEIKISUI CHEMICAL CO LTD) 21 January 1998 (1998-01-21) claim 1; example 1 page 7, line 49 ---	1
A	US 3 515 578 A (TOMITA JUN ET AL) 2 June 1970 (1970-06-02) claims 1,2; example 1 --- -/--	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DATABASE WPI Section Ch, Week 199808 Derwent Publications Ltd., London, GB; Class A21, AN 1998-082826 XP002121608 & JP 09 316306 A (SUMITOMO BAKELITE CO LTD), 9 December 1997 (1997-12-09) abstract -----	1-3

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